Skeletal Formation of Carbocycles with CO₂: Selective Synthesis of Indolo[3,2-*b*]carbazoles or Cyclophanes from Indoles, CO₂, and Phenylsilane

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Supporting Information Placeholder

ABSTRACT: The catalytic reactions of indoles with CO₂ and phenylsilane afforded indolo[3,2-*b*]carbazoles, where the fused benzene ring was constructed by forming two C–H bonds and four C–C bonds with two CO₂ molecules via deoxygenative conversions. Nine-membered cyclophanes made up of three indoles and three CO₂ molecules were also obtained, where the cyclophane framework was constructed by forming six C–H bonds and six C–C bonds. These multi-component cascade reactions giving the completely different carbocycles were switched simply by choosing the solvent, acetonitrile or ethyl acetate.

Organic synthesis with carbon dioxide (CO₂) is a growing research area that is important from the viewpoint of sustainability.¹ However, the diversity of CO₂ fixation reactions is too limited to synthesize a variety of compounds at will. New catalytic reactions need to be developed to expand the variety of CO₂ conversions. Toward this end, reductive CO₂ conversions will play a pivotal role, providing good access to various compounds including fine chemicals.² Hydrogen,³ hydroboranes,⁴ and hydrosilanes⁵ have been used as reductants. Especially, hydrosilanes are useful reductants with moderate reactivity and stability, and the formation of the strong Si-O bond is the thermodynamic driving force for deoxygenative CO₂ conversions. The kinetic barriers in hydrosilylation steps are lowered by catalysts to give silvl formates (HCO₂Si), bis(silyl)acetals (SiOCH₂OSi), methoxvsilanes (CH₃OSi), and/or methane (Scheme 1a),⁶ some of which can be used as reactive intermediates. For example, CO₂ reduction with hydrosilanes in the presence of primary or secondary amines affords N-functionalized products such as formamides and methylamines, where successive C-H and C-N bond-forming reactions occur.⁷ In classifying CO₂ fixation reactions,⁸ we noticed an undeveloped research area producing useful compounds,

such as aldehydes,⁹ alcohols,¹⁰ alkenes,¹¹ alkanes,¹² heterocycles,¹³ and heteroaromatics,¹⁴ via successive C–H and C–C bond formation with CO₂. The development of a variety of CO₂ fixation methods via successive C–H and C–C bond formation will enhance the value of CO₂ as a chemical feedstock.¹⁵

Scheme 1. (a) CO₂ Reduction with Hydrosilanes; (b) Our Previous Work; (c) This Work



We have previously reported the synthesis of diindolylmethane **2a** from 1-methylindole (**1a**), CO₂ (balloon), and phenylsilane (PhSiH₃) in the presence of triphenylborane (BPh₃) under solvent-free conditions at 30 °C, where CO₂ is converted into the methylene group between the two indole rings (Scheme 1b).¹⁶ In the study of the solvent effect, more recently, we have found an unexpected product, indolo[3,2-*b*]carbazole **3a**, in an acetonitrile solution stirred at 40 °C for 48 h (Scheme 1c). The fused benzene ring is constructed between the two indole rings via deoxygenative conversions of two CO₂ molecules, where two C–H bonds and four C–C bonds are formed. Indolo[3,2-*b*]carbazoles are heteroacenes that function as organic semiconductors applicable to organic thin-film transistors,¹⁷ organic photovoltaic cells,¹⁸ and organic light-emitting diodes (OLED),¹⁹ and other functions including biological activity are also known.²⁰ The present catalytic method is simple and easy as compared with the known synthetic methods.²¹ On the other hand, nine-membered cyclophane **4a**, made up of three indoles and three CO₂ molecules, has been selectively produced in ethyl acetate, where six C–H bonds and six C–C bonds are newly formed (Scheme 1c).²² Here we report these multi-component cascade reactions for the first time.

Table 1. Optimization of Reaction Conditions for 3a^a



^{*a*}Reaction conditions: 1-methylindole (**1a**) (1.0 mmol), PhSiH₃ (amount indicated above), BPh₃ (amount indicated above), CO₂ (balloon), MeCN (0.8 mL), 40 °C, 48 h. ^{*b*}Determined by ¹H NMR spectroscopy using mesitylene as an internal standard. ^{*c*}MeCN (0.5 mL). ^{*d*}MeCN (1.0 mL). ^{*e*}30 °C. ^{*f*}50 °C. ^{*g*}Additional heating at 80 °C for 24 h under N₂. ^{*h*}EtOAc instead of MeCN. ^{*i*}B(C₆F₅)₃ instead of BPh₃. 1-Methylindoline (**5a**) was obtained in 40% yield.

We optimized the reaction conditions for the selective synthesis of 3a or 4a from 1a, CO₂, and phenylsilane (Table 1). To examine the effect of the substrate concentration on the yield and selectivity, the amount of acetonitrile was changed (entries 1–3). Although 3a and 4a were

obtained in comparable yields in 0.5 mL of acetonitrile (entry 1), the selectivity of 3a over 4a was remarkably improved by increasing the amount of acetonitrile, and 3a was produced most efficiently in 0.8 mL of acetonitrile (entry 2). The optimal temperature for the formation of 3a was found to be 40 °C (entries 2 and 4–5). When the amount of phenylsilane was changed, the selectivity of 3a over 4a increased dramatically with decreasing the amount of phenylsilane (entries 2 and 6-8). When 1.8 mmol of phenylsilane and 0.25 mmol of BPh₃ were used, **3a** was selectively obtained in 63% yield (entry 9), and the yield of 3a was increased to 73% albeit with lower selectivity by additional heating at 80 °C for 24 h under N_2 (entry 10). Control experiments without BPh₃, phenylsilane, or CO₂ indicated that all of them were essential for the formation of 3a (data not shown). Interestingly, 3a was delivered only when phenylsilane and acetonitrile were employed as reductant and solvent, respectively, while 4a was produced exclusively in ethyl acetate (entry 11) and other solvents (Table S1). In contrast to BPh_3 , $B(C_6F_5)_3$ showed poor catalytic activity, giving neither 3a nor 4a (entry 12); 1-methylindoline (5a) was isolated in 40% yield as observed previously for the solventfree reaction.¹⁶

Under the optimized conditions for 3a (entry 9), a clear slightly yellow solution turned into a deep red solution in 12 h, a pale orange suspension in 24 h, and finally a pale yellow suspension in 48 h (Figure S1). The selective synthesis was crucial for the successful isolation of 3a owing to low solubility in organic solvents. Specifically, 3a and 4a were isolated as follows. A crude reaction mixture was dissolved in chloroform and passed through a short alumina column, and the subsequent reprecipitation with chloroform/hexane afforded 3a in 65% yield as a pale yellow solid, while the filtrate was passed through a silica gel column to give 4a as a white solid in 1% yield (Scheme 2). The structures of **3a** and **4a** were unambiguously determined by X-ray crystallography. ¹³C-Labelled indolo[3,2-b]carbazole 3a' was also synthesized with ¹³CO₂ in 78% yield, and ¹H and ¹³C NMR spectra of **3a'** showed a double doublet at 8.02 ppm (${}^{1}J_{CH} = 160$ Hz, ${}^{4}J_{CH}$ = 3.2 Hz) (Scheme 2) and an intense signal at 98.7 ppm (SI), respectively, which clearly demonstrates that the two carbon atoms at the 6- and 12-positions originated from carbon dioxide. On the other hand, D-labelled indolo[3,2b]carbazole 3a'' was obtained in 53% yield when PhSiD₃ was employed. ¹H NMR spectrum of **3a''** had a small singlet signal at 8.02 ppm, where the ratio of D to H atoms was 95:5 (Scheme 2). This incomplete deuteration is due to the slow exchange of the deuterium atoms of 3a" with the hydrogen atoms of a small amount of water in chloroform. A small amount of D-labelled cyclophane 4a" was also isolated and characterized to confirm that all the hydrogen atoms in the three methylene groups originated from phenylsilane (SI).

Scheme 2. Selective Synthesis of Indolo[3,2-b]carbazoles 3 and Isotope Labeling Experiments^a



^aX-ray crystal structures of **3a**, **4a**, **3k**, **3o**, and **3s** (CCDC 2331185–2331189) are also shown.

Scheme 3. Selective Synthesis of Cyclophanes 4



We next examined substrate scope, adjusting the reaction temperature (Scheme 2). In most cases, indolo[3,2b]carbazoles 3 were isolated by reprecipitation. Nevertheless, 3b-f with electron-donating groups such as the methyl and methoxy groups were obtained in good yields at 35-40 °C. The electron-withdrawing groups such as the halogen atoms and the ester groups were tolerated at 45-50 °C to give 3g-k in modest to good yields. In contrast, the nitro group lowered the reactivity of 11 significantly, resulting in no formation of **31** even at 60 °C, and only diindolylmethane 21 was isolated. All the above results clearly indicate that a more electron-rich indole ring is more favorable for the formation of 3^{23} In addition, the steric effect was also important for the outcome. For example, **3m** was obtained only in a low yield, while **3n** was gained in a good yield. The steric bulkiness of the substituent on the nitrogen atom also affected the productivity of **30-t**. Obviously, this reaction is sensitive to steric hindrance around the reactive sites. On the other hand, cyclophanes **4** were exclusively synthesized in ethyl acetate (Scheme 3). No regioisomers of **3** or **4** were found in all cases.



Figure 1. Time course of the standard reaction of 1a.

Figure 1 shows the time course of the standard reaction of **1a** in acetonitrile as monitored by ¹H NMR spectroscopy. As 1a was consumed, diindolylmethane 2a increased to reach a peak at 10 h, and 3a and 4a then increased with a decrease in 2a. This result suggests that the subsequent reaction of 2a might be the rate-determining step and that **2a** might be a common intermediate leading to 3a and 4a. Several control experiments were performed to gain mechanistic insights (Scheme 4). Under the solvent-free conditions, 1a was converted into 2a in 54% yield without formation of 3a or 4a (Scheme 4a), which suggests that acetonitrile has a pivotal role in the promotion of the whole reaction. When 2a was subjected to the standard reaction, only 4a was obtained in a low yield (Scheme 4b), which might be due to the preferential reaction of 2a with highly reactive species, bis(silyl)acetals. When paraformaldehyde was employed instead of CO₂ and phenylsilane, 3a was not given at all, but 4a was produced from 1a or 2a in modest yields (Schemes 4c and 4d), which strongly suggests that formaldehyde equivalents such as bis(silyl)acetals are used to produce 4a. Considering a possibility that formic acid equivalents might be essential for the formation of 3a, we employed HCO₂Me or CH(OMe)₃, but **3a** was not produced at all (Schemes 4e and 4f). To examine the reactivity of silvl formates, we prepared solutions containing silvl formates in advance; bis(silyl)acetals and methoxysilanes were also generated in different ratios depending on the reaction conditions (Figures S2-S4). Formic acid, formaldehyde, and methanol equivalents were contained in a ratio of 15:1.7:1 (3.04, 0.348, 0.202 mmol) and 51:1.2:1 (4.68, 0.112, 0.091 mmol) in the solutions prepared at 1 atm and 2 MPa CO₂ pressure, respectively; the solution prepared at 2 MPa CO₂ pressure contained more silvl formates and less bis(silyl)acetals.^{24,25} To our delight, **3a** was obtained albeit in 3% and 18% yields by mixing 1a with the solutions prepared at 1 atm and 2 MPa CO₂ pressure, respectively (Schemes 4g and 4h). Furthermore, 3a was

obtained in 32% and 71% yields by mixing **2a** with the solutions prepared at 1 atm and 2 MPa CO₂ pressure, respectively (Schemes 4i and 4j); the reaction of **2a** with silyl formates seems to deliver **3a** most efficiently. Interestingly, cyclic trimer **4a** was also synthesized from dimer **2a** (Schemes 4b, 4i, and 4j), which suggests the fragmentation of **2a**. In fact, a crossover experiment with **2a** and **2d** generated unsymmetrical product **3ad** (Scheme 4k), which strongly suggests the fragmentation of intermediates into, for example, 1-methyl-3-methylidene-3*H*-indolium ions (Scheme 5) during the reaction.

Scheme 4. Control Experiments^a

S	standard reaction								
_	1a	+	CO ₂	+	PhSiH ₃	MeCN	3a (65%)	+	4a (1%)
control reactions									
(a)	1a	+	CO ₂	+	PhSiH ₃	no solvent	<mark>2a</mark> 54%		
(b)	2a	+	CO ₂	+	PhSiH ₃	BPh ₃ MeCN	3a 0%	+	4a 18%
(c)	1a	+	(CH ₂ 0	O) _n		BPh ₃ MeCN, N ₂	3a 0%	+	4a 32%
(d)	2a	+	(CH ₂ 0	O) _n		BPh ₃ MeCN, N ₂	3a 0%	+	4a 26%
(e)	1a	+	HCO or CH	₂Me I(OI	Me) ₃	BPh ₃ MeCN, N ₂	3a 0%	+	4a 0%
(f)	2 a	+	HCO or CH	₂Me I(OI	Me) ₃	BPh ₃ MeCN, N ₂	3a 0%	+	4a 0%
(g)	~~		atm)	1.	PhSiH ₃ , BPh ₃ , MeCN				
	CO	2 (1		2.	1a , N ₂	*	3a 3%	+	2a 38%
(b)	<u> </u>	()		1.	PhSiH ₃ , E	3Ph ₃ , MeCN	30	+	20
(11)		2 (~	ivii aj	2.	1a , N ₂		18%	'	12%
(i)	CO	₂ (1	atm)	1. 2.	PhSiH ₃ , E <mark>2a</mark> , N ₂	3Ph ₃ , MeCN ►	3a 32%	+	4a 13%
(j)	CO	2 (<mark>2</mark>	MPa)	1.	PhSiH ₃ , E	3Ph ₃ , MeCN ►	3a	+	4a
				2.	2a, N ₂		71%		9%
(k)	CO	₂ (<mark>2</mark>	MPa)	1. 2.	PhSiH ₃ , E <mark>2a</mark> , <mark>2d</mark> , N	3Ph ₃ , MeCN	3ad (22%)	+	3a + 3d (29%) (10%)
								Ĺ	Ň
						/	3ad		\searrow
									OMe

^aIsolated yields in parentheses (otherwise NMR yields).

Plausible reaction pathways are shown in Scheme 5. After the generation of 2a from 1a and bis(silyl)acetals (or formaldehyde), the reaction of 2a with silyl formates triggers the fragmentation/addition reactions (or rearrangement) to give a silyl hemiacetal intermediate (or aldehyde), and the subsequent intramolecular electrophilic aromatic substitution and aromatization furnishes 3a. We consider that silyl formates are much less reactive than bis(silyl)acetals and that the former can react only with **2a** having the quite electron-rich aromatic rings. This step may be the rate-determining step, which is consistent with the fact that **2a** was temporarily accumulated (Figure 1). Accordingly, no kinetic isotope effects were observed for the standard reaction of **1a** when a 1:1 mixture of PhSiH₃ and PhSiD₃ was used, which suggests that hydrogen atom transfer is not involved in the rate-determining step. On **Scheme 5. Plausible Reaction Pathways**

the other hand, the reaction of 2a with bis(silyl)acetals and the subsequent cascade reactions via 6a, which has been isolated as a byproduct in solvent-free catalysis,¹⁶ are likely to give 4a. This pathway becomes dominant when bis(silyl)acetals are excessively generated, for example, in ethyl acetate or in the presence of a large amount of phenylsilane.²⁶



In summary, we have selectively synthesized indolo[3,2-b] carbazoles 3 or cyclophanes 4 from indoles 1, CO2, and phenylsilane using BPh3 as a catalyst under mild reaction conditions. In the synthesis of 3, the fused benzene ring was constructed by forming two C-H bonds and four C-C bonds with two CO2 molecules via deoxygenative conversions. In the synthesis of 4, the cyclophane framework was constructed by forming six C-H bonds and six C-C bonds with three CO₂ molecules. These multi-component cascade reactions incorporate two or three CO₂ molecules for the skeletal formation of the carbocycles, which contrasts sharply with other methods for the fixation of multiple CO₂ molecules (mainly, multiple carboxylation).²⁷ The selective construction of the fused benzene ring or cyclophane was achieved by changing the solvent, which is also important from the viewpoint of the switching control of different CO₂ fixation reactions.²⁸ Further work is underway to clarify the reaction mechanism and apply the present method to the synthesis of a variety of compounds.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures and compound data (PDF). CCDC 2331185–2331189 contain the supplementary crystallographic data for this paper.

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ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant No. 20H02780 and 24K01488. We thank Dr. Yukinari Sunatsuki (Okayama University) for X-ray analysis.

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